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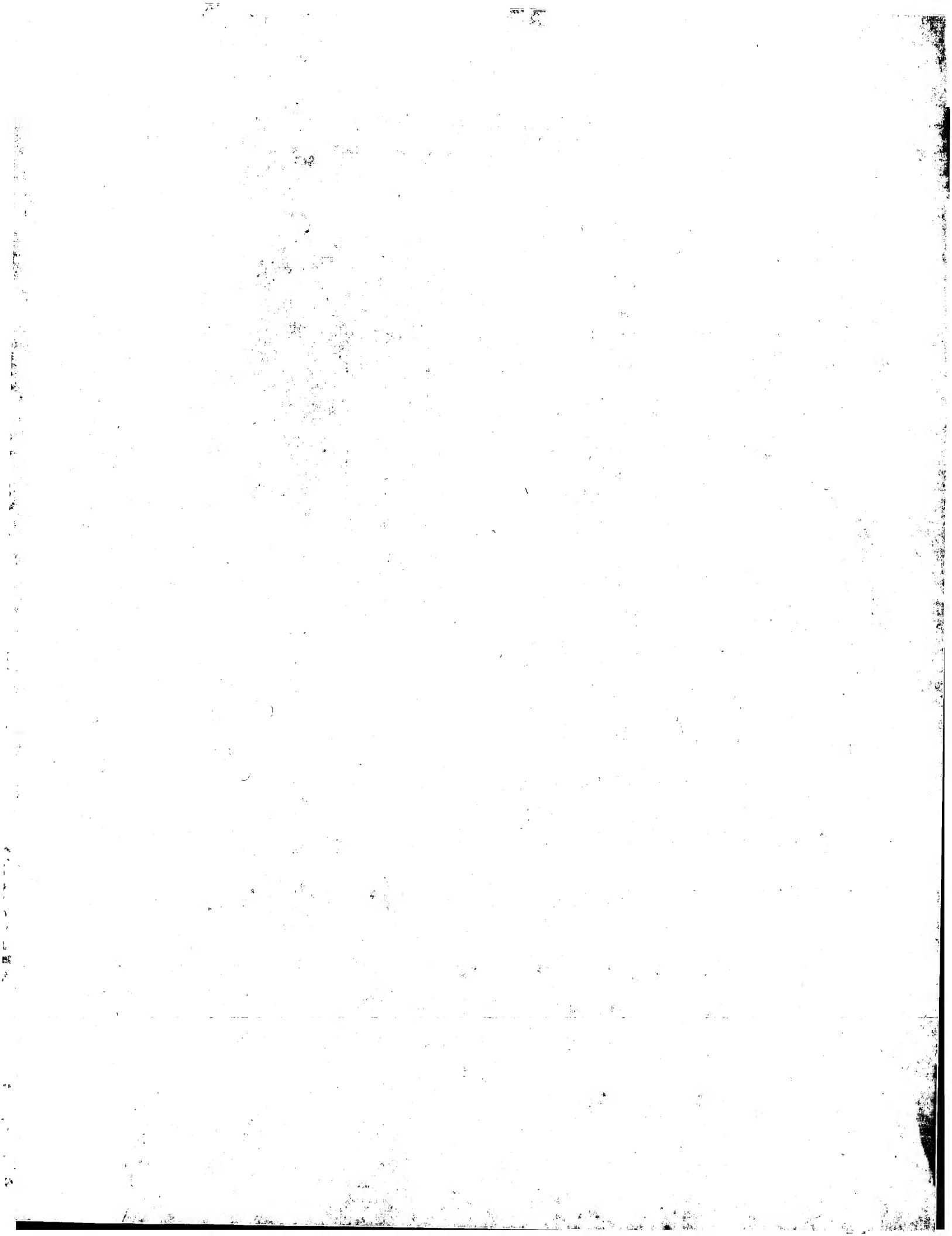
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UK Patent Application GB 2043082 A

(21) Application No 8004187

(22) Date of filing
7 Feb 1980

(30) Priority data

(31) 7903261

(32) 8 Feb 1979

(33) France (FR)

(43) Application published
1 Oct 1980

(51) INT CL³ C08L 31/02
39/06 //
A61K 7/06

(52) Domestic classification
C3P 154 156 158 174
252 302 304 306 330

FE

A5B FC

C3Y B101 B230 B240

B243 B245 F620

(56) Documents cited

GB 943172

GB 828970

(58) Field of search

C3P

C3V

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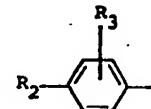
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Messrs J A Kemp & Co

(54) **Copolymers of n-vinylpyrrolidone and a vinyl, allyl or methacryl ester of an α - or β -cyclic carboxylic acid, and their use in cosmetics**

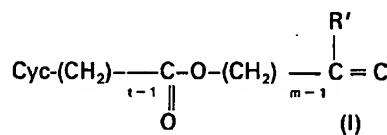
in which R₁ represents hydrogen or methyl and p is 1 or 2,

(iii) a radical of the formula:



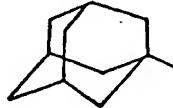
in which R₂ represents hydrogen, methyl, ethyl, tert.-butyl, ethoxy, butoxy or dodecoxy and R₃ represents hydrogen, C₁₋₄ alkyl or C₁₋₄ alkoxy, or

(iv) a radical of the formula:

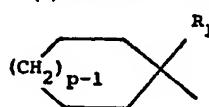


in which R' represents hydrogen or methyl, m is 1 or 2 and t is 1 or 2 such that if t = 1, Cyc represents:

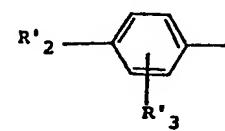
(i) a radical of the formula:



(ii) a radical of the formula:



and if t = 2, Cyc represents a radical of the formula:



in which R'₂ and R'₃ are as defined under R₂ and R₃, respectively.

GB 2043082 A

SPECIFICATION

Copolymers of N-vinylpyrrolidone and a vinyl, allyl or methallyl ester of an α - or β -cyclic carboxylic acid, and their use in cosmetics

5 The present invention relates to copolymers of N-vinylpyrrolidone and a vinyl, allyl or methallyl ester of an α - or β -cyclic carboxylic acid; these copolymers can be used in cosmetics, in particular in lacquers and wavesetting lotions.

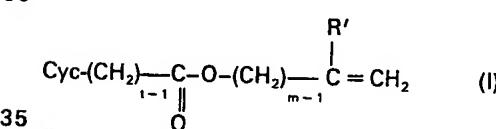
10 Polyvinylpyrrolidone (PVP), which forms a film which is both elastic and strong, has been widely used in cosmetic formulations such as lacquers and wavesetting lotions.

15 However, the use of polyvinylpyrrolidone has only proved totally satisfactory when the atmospheric humidity is relatively low. In fact, polyvinylpyrrolidone possesses a certain hygroscopicity, such that, after a certain time in a humid atmosphere, the polyvinylpyrrolidone film tends to become sticky. To overcome the hygroscopicity of polyvinylpyrrolidone, it has been proposed to use copolymers of N-vinyl-pyrrolidone and vinyl acetate. These copolymers are less sensitive to atmospheric humidity and furthermore possess good fixing properties. By varying the proportion of vinyl acetate, it is possible to influence some of the properties of the film, in particular the hardness and the hygroscopicity.

20 However, these copolymers of N-vinylpyrrolidone and vinyl acetate do not always possess a very good lacquering ability and can be relatively brittle.

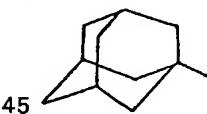
25 The present invention is intended to overcome the disadvantages of the films produced from N-vinylpyrrolidone, by providing copolymers obtained by polymerising N-vinylpyrrolidone with at least one vinyl, allyl or methallyl ester of an α - or β -cyclic carboxylic acid. In fact, it has been found that by polymerising N-vinylpyrrolidone with this type of ester, the copolymers obtained possess excellent properties, in particular cosmetic properties, that is to say moderate hardness, very low hygroscopicity, good lacquering ability and a pleasant feel.

30 The present invention provides polymers which contain units resulting from the polymerisation of (a) N-vinylpyrrolidone with (b) at least one vinyl, allyl or methallyl ester of an α - or β -cyclic carboxylic acid, corresponding to the following formula:

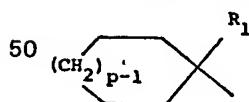


35 in which R' represents a hydrogen atom or a methyl radical, m is 1 or 2 and t is 1 or 2; such that if $t = 1$, Cyc represents a monocyclic or polycyclic, saturated or unsaturated radical such as:

40 (i) a radical of the formula:

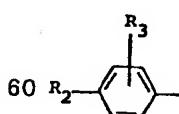


45 (ii) a radical of the formula:



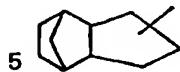
50 in which R_1 represents a hydrogen atom or a methyl radical and p is 1 or 2,

55 (iii) a radical of the formula:

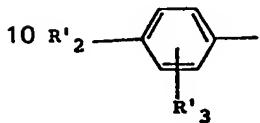


60 in which R_2 represents a hydrogen atom or a methyl, ethyl, tert.-butyl, ethoxy, butoxy or dodecoxy radical and R_3 represents a hydrogen atom, an alkyl radical having 1 to 4 carbon atoms or an alkoxy radical having 1 to 4 carbon atoms, or

(iv) a radical of the formula:



and if $t = 2$, Cyc represents a radical of the formula:



15 in which R'_2 and R'_3 are as defined under R_2 and R_3 , respectively.

Amongst the vinyl, allyl or methallyl esters of the formula (I), the following may be mentioned in particular: the vinyl, allyl and methallyl esters of adamantine-1-carboxylic acid, cyclohexane-

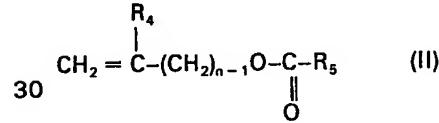
carboxylic acid, cyclopentane-carboxylic acid, benzoic acid, phenylacetic acid, 4-tert.-butylbenzoic acid, 1-methylcyclopentane-1-carboxylic acid, 1-methylcyclohexane-1-carboxylic acid, tricy-

20 clo[5.2.1.0^{2,6}]decane-3-carboxylic acid and tricyclo[5.2.1.0^{2,6}]decane-4-carboxylic acid, these last two acids being sold, in the form of a mixture, by HOECHST, under the tradename TCD

Carboxylic Acid S.

The copolymers according to the invention can also contain units of at least one other monomer which is:

25 1. A vinyl, allyl or methallyl ester of the formula:



in which n is 1 or 2, R_4 represents a hydrogen atom or a methyl radical and R_5 represents a linear or branched alkyl radical having from 1 to 21 carbon atoms.

35 Amongst the esters of the formula (II), the following may be mentioned in particular: the vinyl, allyl and methallyl esters of acetic acid, propionic acid, butyric acid, pivalic acid, hexanoic acid, octanoic acid, decanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, behenic acid, 2-ethyl-hexanoic acid, 2,2-dimethylpentanoic acid, 2,2-dimethyl-hexanoic acid, 2,2-dimethyloctanoic acid, 2,2-dimethyl-decanoic acid, 2,2,4,4-tetramethylvaleric acid, 2-

40 isopropyl-2,3-dimethylbutyric acid, 2-methyl-2-ethylheptanoic acid, 2-methyl-2-propylhexanoic acid, 2-methyl-2-isopropylhexanoic acid, 3,5,5-trimethylhexanoic acid and their isomers, and also mixtures thereof and in particular the mixture sold by SHELL under the tradename "Versatic Acid" and the mixtures sold by UGINE-KUHLMANN under the tradenames "CEKANOIC C₈, C₉ and C₁₀ Acids".

45 2. A vinyl ether of the formula:



in which R_6 represents a linear or branched alkyl radical having from 6 to 18 carbon atoms.

50 Amongst the vinyl ethers of the formula III, the following may be mentioned: hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, dodecyl vinyl ether, hexadecyl vinyl ether and octadecyl vinyl ether, or

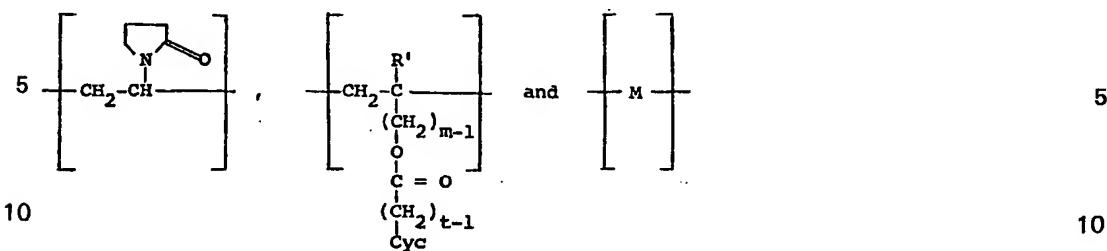
3. An α -olefine of the formula:



in which s is an integer from 3 to 15.

Amongst the α -olefines of the formula IV, the following may be mentioned: hex-1-ene, oct-1-ene, dec-1-ene, dodec-1-ene and octadec-1-ene.

60 The copolymers according to the invention can generally be represented as having recurring units of the following general formula:



in the relative amounts, x, y and z respectively, in which Cyc, R', m and t are as defined above, M is a unit derived from at least one monomer as represented by the formulae (II) to (IV) above,

15 x represents from 20 to 90%, and preferably from 25 to 80%, by weight, y represents from 1 to 70%, and preferably from 10 to 50%, by weight, and z represents from 0 to 70%, and preferably from 10 to 60% by weight.

However, it is important to note that the sum of the non-homopolymerisable monomers should not exceed 50 mol% of the total of the monomers. The non-homopolymerisable

20 monomers according to the invention are:

- (i) the compounds of the formula (I) when m = 2,
- (ii) the compounds of the formula (II) when n = 2, and
- (iii) the compounds of the formulae (III) and (IV).

25 Preferably, when m = 2 in the monomers of the formula (I), the mol percentages for x, y and z are as follows: x represents from 50 to 90%, y represents from 10 to 50% and z represents from 0 to 40%.

The copolymers according to the invention, as defined above, generally have an average molecular weight from 5,000 to 60,000 and more particularly from 10,000 to 45,000, these molecular weights being number-average molecular weights determined by osmometry.

30 The present invention also provides a process for the preparation of the copolymers. They can be prepared by the conventional methods of polymerisation, that is to say either in solution in a solvent, or in bulk, or also in suspension in an inert liquid, or in emulsion.

35 The polymerisation reaction can also be carried out in suspension in water saturated with sodium chloride, in the presence of a protective colloid or suspending agent, such as polyvinyl alcohol, cross-linked polyacrylic acid or the product known under the tradename Cellosize WP-09; this makes it possible to obtain the polymer in the form of beads at the end of the reaction.

40 The polymerisation initiators which can be used in the polymerisation process are preferably azo-bis-iso-butyronitrile, peresters, percarbonates or oxidation/reduction systems, these initiators being used either singly or as a mixture.

45 The amount of the initiator is generally from 0.1 to 6% by weight relative to the total weight of the monomers used for the copolymerisation.

The polymerisation reaction is preferably carried out at a temperature from 45 to 100°C and more particularly at the reflux temperature of the reaction mixture.

45 The reaction time is preferably from 6 to 24 hours.

The present invention also provides a cosmetic composition which contains at least one copolymer according to the invention as a resin, these compositions being presented in the form of wavesetting lotions, aerosol lacquers, rinses or shampoos.

50 According to the invention, the cosmetic compositions generally contain from 0.5 to 10% by weight of at least one copolymer of this invention.

55 The wavesetting lotions according to the invention are usually in the form of aqueous solutions or aqueous-alcoholic solutions containing from 20 to 70% by weight of alcohol, and have a copolymer concentration which is preferably from 1 to 3% by weight.

The alcohols which are generally used for producing these wavesetting lotions are preferably 55 low molecular weight lower aliphatic alcohols such as ethanol or isopropanol.

The aerosol hair lacquers according to the invention can be obtained by dissolving, in an alcohol, at least one copolymer of this invention, this solution being placed in a pressurised or non-pressurised container.

60 According to this embodiment, the copolymer is preferably used in an amount from 0.7 to 8% by weight.

The aerosol lacquers can also contain an auxiliary solvent which is suitably present in an amount from 3 to 35% by weight.

Amongst these auxiliary solvents, the following may be mentioned in particular; methylene chloride, trichloroethane, ethyl chloride, acetone, ethyl acetate and dichlorodifluoroethane.

65 In the aerosol lacquers according to the invention, the alcohol, which can be either ethanol or

isopropanol, is generally present in an amount of 5 to 80%, and preferably 6 to 70%, by weight.

Propellants which can be used in particular for the aerosol lacquers are fluorochlorinated hydrocarbons, either used singly or as a mixture, especially those known under the tradenames 5 "Freon" and in particular "Freons 11, 12, 22, 133A and 142b".

5

Propellants which can also be used are carbon dioxide, nitrous oxide (N₂O), dimethyl ether and hydrocarbons such as propane, butane and isobutane, these propellants being used either singly or as a mixture with one another or with one or more "Freons".

When the compositions are in the form of shampoos, they contain, in addition to the polymer 10 according to the invention, at least one anionic, cationic or non-ionic surface-active agent.

10

The compositions according to the invention can also contain various ingredients which are generally used in this type of composition, such as plasticisers, agents for imparting gloss, perfumes, dyestuffs and restructuring agents.

The following examples further illustrate the present invention:—

15

15 PREPARATION EXAMPLES

EXAMPLE 1

A solution of 35 g of vinyl 4-tert.-butyl-benzoate, 35 g of vinyl acetate, 30 g of N-vinylpyrrolidone and 0.2 g of azo-bis-isobutyronitrile in 300 g of ethanol is introduced into a 20 round-bottomed flask equipped with a condenser, a mechanical stirrer and a nitrogen inlet.

20

The mixture is subsequently heated under reflux for 24 hours, whilst stirring, and the polymer is then precipitated in ethyl ether. After filtration, the polymer is dried at 50°C under reduced pressure.

The yield is 42% and the polymer obtained has a viscosity of 1.56 cP, measured in a 5% 25 strength solution in dimethylformamide (DMF) at 34.6°C.

25

EXAMPLE 2

30 g of N-vinylpyrrolidone, 15 g of vinyl cyclohexanoate, 55 g of vinyl acetate, 0.5 g of tert.-butyl 2-ethylhexanoate and 25 g of ethanol are introduced into a round-bottomed flask 30 equipped with a condenser, a mechanical stirrer and a nitrogen inlet.

30

The mixture is subsequently heated under reflux for 24 hours, whilst stirring, and then, when the polymerisation reaction is complete, the polymer is precipitated in ethyl ether.

After filtration, the polymer is dried at 50°C under reduced pressure.

The yield is 80% and the polymer obtained has a viscosity of 2.4 cP, measured in a 5% 35 strength solution in dimethylformamide (DMF) at 34.6°C.

35

The copolymers in Table I were also prepared in accordance with the procedures described in Example 1 and 2 above:

TABLE 1

Monomer % by weight	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
N-vinylpyrrolidone	*	*	*	*	*	*	*	*	*	*	*	*
vinyl 4-tert.-butylbenzoate	70	50	30	70	50	40	30	35	40	40	30	35
allyl 4-tert.-butylbenzoate	30	50	70	15	25	10	15	15	5	5	15	12
vinyl benzoate												
vinyl cyclopentanoate												
vinyl phenylacetate												
allyl benzoate												
vinyl acetate	15	25	50	50	45	45	45	45	40	50	50	38
vinyl propionate												
allyl propionate												
allyl stearate												
octadecyl vinyl ether												
decadecyl vinyl ether												
Yield %	80	62	26	73.2	70	40	42	55	48	59	92	64
Viscosity (5% strength solution in DMF at 34.6 °C)	2.05	1.89	1.67	1.88	1.54	1.52	1.82	1.69	1.54	1.68	2.3	1.73

*obtained in accordance with the process of Example 1

**obtained in accordance with the process of Example 2

COMPOSITION EXAMPLES**EXAMPLE A**

An aerosol lacquer is prepared according to the invention by packaging the following ingredients in a container:

5	Copolymer prepared in accordance with Example 1	3 g	5
	Ethanol (or isopropanol)	40 g	
	Methylene chloride	20 g	
	Propellant: mixture of 35% of propane and		
10	65% of butane	40 g	10

In this example, the copolymer prepared in accordance with Example 1 can be replaced by the same amount of the copolymer prepared in accordance with Example 4.

15	EXAMPLE B		15
	An aerosol lacquer is prepared according to the invention by mixing the following ingredients:		

	Copolymer prepared in accordance with Example 3	3 g	
	Ethanol	60 g	
20	Propellant: mixture of 35% of propane and		20
	65% of butane	40 g	

EXAMPLE C

25	An aerosol lacquer is prepared according to the invention by mixing the following ingredients:		25
	Copolymer prepared in accordance with Example 2		

	Ethanol q.s.p.	7.6 g	
		100 g	

22 g of the composition thus obtained are then packaged in an aerosol container together with 78 g of a 61.5/38.5 mixture of Freon 11 and Freon 12.

When this lacquer is applied to the hair, no powder formation is observed with time and the hair does not become sticky, even in a humid atmosphere.

35	EXAMPLE D		35
	A wavesetting lotion is prepared according to the invention by mixing the following ingredients:		

	Polymer prepared in accordance with Example 4	2 g	
	Perfume	0.15 g	
40	Ethanol	46 g	40
	Water q.s.p.	100 g	

In this example, the polymer prepared in accordance with Example 4 can advantageously be replaced by the same amount of one of the polymers prepared in accordance with Examples 5 to 8 or 14.

After this wavesetting lotion has been applied to the hair, the latter is wound onto wavesetting rollers and then dried. The waveset holds very well with time and there is no powder formation.

50	EXAMPLE E		50
	A wavesetting lotion is prepared according to the invention by mixing the following ingredients:		

	Copolymer prepared in accordance with Example 9	3.5 g	
	Perfume	0.2 g	
55	Sufficient dyestuff to colour the lotion	0.15 g	55
	Isopropyl alcohol	50 g	
	Water q.s.p.	100 g	

When applied in the conventional manner, this wave setting lotion makes it possible to impart, to the hair, a glossy appearance and an excellent hold with time.

In this example, the polymer prepared in accordance with Example 9 can advantageously be replaced by the same amount of one of the polymers prepared in accordance with Examples 10 to 12.

65	EXAMPLE F		65

A rinsing product or "rinse", in the form of an emulsion, is prepared according to the invention by mixing the following ingredients:

5	Liquid petrolatum	9.6 g	
	Polyglycerolated fatty alcohols ($C_{16}C_{18}$) (containing 2 to 6 mols of glycerol)	6.5 g	5
	Polymer prepared in accordance with Example 13	1.5 g	
	Water q.s.p.	100 g	

10 This product is applied to hair which has been washed and towel-dried, by spreading it carefully over the whole head of hair. After a few minutes have elapsed, the hair is carefully rinsed.

The hair is glossy and easy to comb out.

15 In this example, the polymer according to Example 13 can advantageously be replaced by the same amount of one of the polymers prepared in accordance with Examples 2 to 5 and 8.

15

EXAMPLE G

An ionic shampoo is prepared according to the invention by mixing the following ingredients:

20	Triethanolamine lauryl-/myristyl-sulphate	12 g	20
	Copra diethanolamide	2 g	
	Myristyldimethylamine oxide	1.5 g	
	Copolymer prepared in accordance with Example 10	1.5 g	
	Lactic acid q.s.p. pH = 6.5	1.5 g	
25	Water q.s.p.	100 g	25

EXAMPLE H

A cationic shampoo is prepared according to the invention by mixing the following ingredients:

30	Cetyltrimethylammonium bromide	2 g	30
	Polyglycerolated lauryl alcohol containing 4 mols of glycerol	12 g	
	Polymer prepared in accordance with Example 6	1 g	
35	Perfume	0.2 g	35
	Lactic acid q.s.p. pH = 4.5		
	Water q.s.p.	100 g	

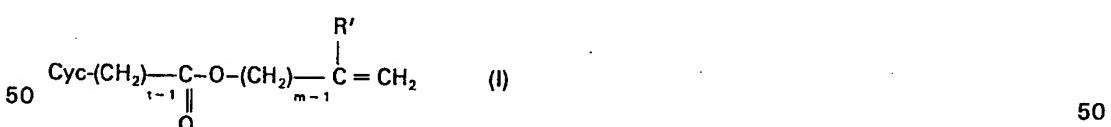
40 In this example, the polymer prepared in accordance with Example 6 can advantageously be replaced by the same amount of one of the polymers prepared in accordance with Examples 7 or 13.

40

CLAIMS

45 1. A copolymer derivable from the polymerisation of (a) N-vinylpyrrolidone and (b) at least one vinyl, allyl or methallyl ester of an α - or β -cyclic carboxylic acid of the formula:

45



in which R' represents a hydrogen atom or a methyl radical, m is 1 or 2 and t is 1 or 2 such that if t = 1, Cyc represents:

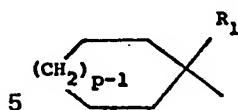
55 (i) a radical of the formula:

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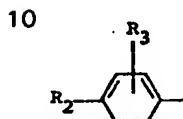
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(ii) a radical of the formula:



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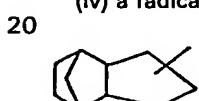
in which R₁ represents a hydrogen atom or a methyl radical and p is 1 or 2,
 (iii) a radical of the formula:



10

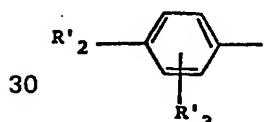
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in which R₂ represents a hydrogen atom or a methyl, ethyl, tert.-butyl, ethoxy, butoxy or dodecoxy radical and R₃ represents a hydrogen atom, an alkyl radical having 1 to 4 carbon atoms or an alkoxy radical having 1 to 4 carbon atoms, or
 (iv) a radical of the formula:



20

25 and if t = 2, Cyc represents a radical of the formula:



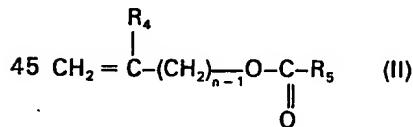
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in which R'₂ and R'₃ are as defined under R₂ and R₃ respectively.

2. A copolymer according to claim 1, in which the said ester is a vinyl, allyl or methallyl ester of adamantan-1-carboxylic acid, cyclohexanecarboxylic acid, cyclopentane-carboxylic acid, 35 benzoic acid, phenylacetic acid, 4-tert.-butylbenzoic acid, 1-methylcyclopentane-1-carboxylic acid, 1-methylcyclohexane-1-carboxylic acid, tricyclo[5.2.1.0^{2,6}]decane-3-carboxylic acid or tri-cyclo[5.2.1.0^{2,6}]decane-4-carboxylic acid.

3. A copolymer according to Claim 1 or 2 which is also derivable from at least one other 40 monomer which is:

(i) a vinyl, allyl or methallyl ester of the formula:



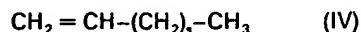
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in which n is 1 or 2, R₄ represents a hydrogen atom or a methyl radical and R₅ represents a 50 linear or branched alkyl radical having from 1 to 21 carbon atoms,
 (ii) a vinyl ether of the formula:



50

55 in which R₆ represents a linear or branched alkyl radical having from 6 to 18 carbon atoms, or
 (iii) an α -olefine of the formula:



55

60 in which s is an integer from 3 to 15.

4. A copolymer according to any one of the preceding claims, which comprises units of the following formulae

60

